

Laser-markable plastics

The present invention relates to laser-markable plastics of which a feature is that a plastic which is difficult to laser-treat comprises as absorber material one or more intrinsically laser-markable polymers in the form of micromilled particles having a particle size of 0.1 - 100 μm .

The labelling of production goods is becoming increasingly important in almost all sectors of industry. For example, it is frequently necessary to apply production dates, expiry dates, barcodes, company logos, serial numbers, etc. At present, these marks are predominantly made using conventional techniques such as printing, embossing, stamping and labelling. However, the importance of contactless, high-speed and flexible marking using lasers is increasing, especially in the case of plastics. This technique makes it possible to apply graphic inscriptions, for example barcodes, at high speed even on a non-planar surface. Since the inscription is within the plastics article itself, it is durable and resistant to abrasion.

Many plastics, for example polyethylene (PE), polypropylene (PP), polyamide (PA), polymethyl methacrylate (PMMA), polyoxymethylene (POM), polyurethane (PUR), polyesters have hitherto proved to be very difficult or even impossible to mark by means of the laser. A CO_2 laser which emits light in the infrared region at 10.6 μm produces only a faint, barely legible mark on polyolefins, even at very high output levels, since the absorption coefficient of the plastics to be processed is not high enough at these wavelengths to induce a colour change in the polymeric material. The plastic must not completely reflect or transmit the laser light, since if it did there would be no interaction. However, there must also not be strong absorption, since in that case the plastic evaporates to leave only an engraving. The absorption of the laser beams and hence the interaction with the material

depends on the chemical structure of the plastic and on the laser wavelength employed. In many cases it is necessary to add appropriate additives, for example absorbers, in order to render plastics laser-inscribable.

The article "Pearl Lustre Pigments - Characteristics and Functional Effects" in Speciality Chemicals, May 1982, Vol.2, No. 2 discloses the use of pearl lustre pigments for laser marking. Pearl lustre pigments, however, have the disadvantage that they severely alter the colour properties of the plastic, an effect which is often unwanted.

DE-A 29 36 926 discloses that the inscription of a polymeric material by means of laser light can be achieved by adding to the plastic a filler, such as carbon black or graphite, which discolours on exposure to energetic radiation.

EP 0 190 997 A prepares laser-inscribable moulding compounds, including PE, ~~PE-[sic]~~ or PS, by adding at least one inorganic pigment to the high molecular mass organic material.

In EP 0 330 869, TiO_2 and carbon black are added to PBT and PET. The inscription is dark on a light background. The use of carbon black and/or graphite as absorbers in connection with the laser marking of polyesters is known from EP 0 485 181.

However, the fillers known for laser marking have the disadvantage either that they permanently colour the plastic that is to be inscribed, and hence the laser inscription, which is usually a dark script on a lighter background, then lacks sufficient contrast, i.e. legibility, or that as in the case, for example, of kaolin the mark is very faint and becomes readily visible only when large amounts of the additive are employed.

DE 195 36 047 describes the use of polycarbonate, which itself is difficult to laser-mark owing to its amorphous structure, in a polymer matrix of a polyalkylene terephthalate. Through absorption of

laser energy it is possible for dark characters to be achieved on a light background in the polymer matrix of a polyalkylene terephthalate.

In addition to the abovementioned plastics, however, there are also polymers which can be marked by means of a laser with darkness and great contrast without the addition of additives. Examples of such polymers include PET, butadiene-styrene (ABS), polystyrene, polyphenyl ether (PPO), liquid crystal polymers (LCP), polyphenylene sulfide, polyarylates, polyaryl sulfides, polyaryl sulfones, polyaryl ether ketones, and blends thereof.

The object of the present invention, therefore, was to find laser-markable plastics which permit high-contrast laser marking on exposure to laser light. In this context, the filler or successful absorber should have a very pale, neutral inherent colour and should possess the properties of the precoloured plastic that is to be marked or should have little or no effect on these properties.

It has surprisingly been found that a plastic which is difficult to laser-treat can be marked very effectively if, for example, one of the abovementioned intrinsically markable polymers is added in fine distribution to the plastic. The intrinsic markability of the polymer is thus transferred to the plastic which shows little if any such behaviour. Following laser bombardment, a plastic doped in this way shows high-contrast and crisply contoured markings even at low laser intensities.

The invention therefore provides laser-markable plastics, characterized in that plastics which are difficult to laser-treat comprise one or more intrinsically markable polymers having a particle size of from 0.1 to 100 μm .

Through the addition of micromilled, intrinsically markable polymers as absorbers in concentrations of 0.1 to 10% by weight, preferably 0.1 to 5% by weight and, in particular, 0.1 to 2% by

*polymer/absorber
concentration*

weight, based on the plastics system, a high contrast is obtained in connection with laser marking. The concentration of the intrinsically markable polymers in the plastic, however, is dependent on the plastics system employed and on the laser used.

Suitable polymers or polymer mixtures are all known readily laser-treatable plastics, such as PET, ABS, polystyrene, PPO, polyphenylene sulfide, polyphenylene sulfone, polyimidosulfone and LCPs, for example.

Micromilled thermoplastics having a very high melting range of $>300^{\circ}\text{C}$ are particularly suitable. The crispness of the contours of the mark is determined in particular by the particle size of the micromilled polymers. The polymers preferably have particle sizes in the range from 0.1 to 50 μm , in particular from 1 to 20 μm .

The resulting mark is positively influenced if the intrinsically markable polymer comprises as further absorber, a light-sensitive pigment, such as a filler, for example, a conductive pigment and/or a special-effect pigment. The addition of a further absorber intensifies the contrast as a function of the plastics system used. The amount of light-sensitive pigment added should be between 0.1 and 90%

Particularly suitable light-sensitive pigments are fillers, such as TiO_2 and SiO_2 , for example, and phyllosilicates. Suitable silicatic platelets here are, in particular, light-coloured or white micas. It is of course also possible to use other natural micas, such as phlogopite and biotite, synthetic mica, talc flakes and glass flakes. By special-effect pigments are meant all known lustre, metallic and pearl lustre pigments, as marketed, for example, by the companies Mearl, Eckart-Werken and Merck KGaA. Examples of suitable conductive pigments are the pigments marketed under the tradename Minatec® by Merck KGaA. These are platelet-shaped TiO_2 /mica pigments comprising an external tin/antimony oxide layer as conductive coat. Other

suitable light-sensitive pigments are the oxides, hydroxides, sulfides, sulfates and phosphates of metals such as copper, bismuth, tin, zinc, silver, antimony, manganese, iron, nickel and chromium, for example.

- 5 Particular mention should be made in this case of the use of antimony, bismuth oxychloride and basic copper(II) hydroxide phosphate. Particular preference in this context is given to a product as formed by heating blue Cu(II) orthophosphate ($\text{Cu}_3(\text{PO}_4)_2 \cdot 3 \text{H}_2\text{O}$) by
- 10 heating ~~to~~ to from 100 to 200°C, and which has the empirical chemical formula 4 $\text{CuO} \cdot \text{P}_2\text{O}_5 \cdot \text{H}_2\text{O}$ or $\text{Cu}_3(\text{PO}_4)_2 \cdot \text{Cu}(\text{OH})_2$. Other suitable copper phosphates are 6 $\text{CuO} \cdot \text{P}_2\text{O}_5 \cdot 3 \text{H}_2\text{O}$, $\text{Cu}_3(\text{PO}_4)_2 \cdot 3 \text{Cu}(\text{OH})_2$, 5 $\text{CuO} \cdot \text{P}_2\text{O}_5 \cdot 3 \text{H}_2\text{O}$, $\text{Cu}_3(\text{PO}_4)_2 \cdot 2 \text{Cu}(\text{OH})_2 \cdot \text{H}_2\text{O}$, 4 $\text{CuO} \cdot \text{P}_2\text{O}_5$, 4 $\text{CuO} \cdot \text{P}_2\text{O}_5 \cdot 3\text{H}_2\text{O}$, 4
- 15 $\text{CuO} \cdot \text{P}_2\text{O}_5 \cdot 1.5 \text{H}_2\text{O}$, 4 $\text{CuO} \cdot \text{P}_2\text{O}_5 \cdot 1.2 \text{H}_2\text{O}$.

An improvement in laser markability is also achieved if, in addition to the intrinsically marking polymer, one or more abovementioned light-sensitive pigments are added as a further component to the

20 plastic. In this case the proportion by weight of all absorbers in the plastic, in combination with the micromilled polymers, should not exceed a total of 10% by weight, based on the plastics system. The plastic preferably contains 0-5% by weight of light-sensitive

25 pigments, especially 0-1% by weight. In this context, there is no restriction on the proportion in which the light-sensitive pigments are mixed with the micromilled polymers.

It is also possible to add, to the plastic that is difficult to laser-treat, colour pigments, which permit colour variations of any type and at the same time ensure that the laser marking is retained.

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The light-sensitive pigments and/or colour pigments are added preferably together with the polymers, although separate addition is also possible in principle. A mixture of different light-sensitive pigments can also be added to the plastic.

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Marking is preferably carried out using high-energy radiation, generally in the wavelength range

from 150 nm to 10,600 nm, in particular in the range from 150 nm to 1100 nm. Mention may be made here, for example, of CO₂ lasers (10,600 nm), Nd:YAG lasers (1064 nm or 532 nm) or pulsed UV lasers (excimer lasers). Particular preference is given to the use of Nd:YAG lasers (1064 nm and 532 nm) and CO₂ lasers (10,600 nm). The energy densities of the lasers employed are generally in the range from 0.3 mJ/cm² to 50 J/cm², preferably in the range from 0.3 mJ/cm² to 10 J/cm².

All known plastics which can only be laser-marked with great difficulty, as are described, for example, in Ullmann, Vol. 15, p. 457 ff., ~~Vol. 15~~ [sic], Verlag VCH or Saechtling Kunststoff Taschenbuch, can be employed for laser marking through addition of the polymers of the invention. Examples of such plastics are thermosets, polyethylene (PE-HD, PE-LD, PE-LLD), polypropylene (PP), polyesters, polyacetal, polyamides (PA), polyurethanes (PUR), polybutylene terephthalate, polymethyl methacrylate (PMMA), polyvinyl acetal, polystyrene, butadiene-styrene (ABS), acrylonitrile-styrene-acrylate (ASA), and their copolymers and/or mixtures thereof. In particular, polyolefins, polyurethanes, polyoxymethylenes and polyamides, owing to their mechanical properties, the cost-effective processing methods and their poor laser-markability, are suitable for doping with the polymers of the invention.

The incorporation of the micromilled polymer into the plastic takes place by the techniques known for pigments and fillers. Subsequently, the pigmented plastic is then deformed under the action of heat. When choosing the intrinsically markable polymer to be milled it should be borne in mind that the particle structure is retained following the incorporation; in other words, the particles should not be soluble in the melt, and should not melt as well. This is achieved by appropriate tailoring of the melting ranges of the plastics system to that of the micromilled polymer.

When the micromilled polymer is incorporated into the plastics granules it is possible, if desired, to add coupling agents, organic, polymer-compatible solvents, stabilizers, optical brighteners, colour pigments, dyes, fillers, reinforcing agents, flameproofing additives, antistatics and/or surfactants which are temperature-stable under the operating conditions. In addition to the auxiliaries customarily employed it is possible to add further additives, not mentioned here, to the plastic. The presence of further additives in the existing plastics systems, however, may exert an effect on the marking result.

The plastics granule/polymer mixture is generally prepared by charging an appropriate mixer with the plastics granules, wetting them with any additives, and then adding the micromilled polymers and mixing them in. The mixture obtained in this way can then be processed directly in an extruder or an injection moulding machine. The mouldings formed in the course of processing usually exhibit a very homogeneous distribution of the polymers or of the polymer mixture. Finally, laser marking takes place, preferably with a Nd:YAG laser.

Inscription with the laser is carried out by introducing the sample into the beam path of a pulsed laser, preferably a Nd:YAG laser. Inscription with a CO₂ laser or an excimer laser is also possible. However, the desired results can also be achieved with other types of laser featuring a wavelength in a range of high absorption by the intrinsically marking polymer. The resulting shade and depth of colour are determined by the laser parameters, such as the irradiation time and irradiation output. The output of the lasers used depends on the particular application and can be determined regularly in each individual case by the skilled worker.

The plastic doped in accordance with the invention can be used in all sectors where customary printing processes have hitherto been employed for the

Additives
to the plastic
+ micromilled
polymer

Injection
Moulding

inscription of plastics. For example, mouldings of the plastic of the invention can be employed in the electrical, electronic and motor vehicle industry. The labelling and inscription of, for example, housings, lines, keycaps, transcripts or functional parts in the heating, ventilation and cooling sectors, or switches, plugs, levers and handles which consist of the plastic of the invention, can be marked ~~here~~ with the aid of laser light, even at difficult-to-reach points. Owing to its low heavy-metal content, the plastics system of the invention can also be employed in packaging in the foodstuffs sector or in the toy sector. The markings on packaging are notable for their resistance to wiping and scratching, for their stability during subsequent sterilization processes, and for the fact that they can be applied in a hygienically pure manner in the marking process. Complete label motifs can be applied durably to the packaging for a reusable system. Another important area of application for laser inscription is that of identity cards and plastic tags for the individual identification of animals: so-called cattle tags or earmarks. The laser marking of plastics articles or mouldings which consist of the plastic of the invention is hence possible.

The examples which follow are intended to illustrate the invention without, however, restricting it.

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Examples

Example 1

- 5 99 parts of polypropylene (Stamylan PPH 10 from DSM)
 1 part of polyphenylene sulfide milled to a particle
 size < 25 μm

 The components are physically mixed and by
means of an injection moulding machine are homogenized
10 and shaped to form platelets. The inscription with a
Nd:YAG laser at 532 and 1064 nm wavelengths shows a
high-contrast black marking with a smooth surface over
a wide range of settings.

15 Example 2

- 99.5 parts of polypropylene (Stamylan PPH 10)
 0.5 part of polyphenylene sulfone milled to a
 particle size < 10 μm

20 The components are mixed and by means of an
injection moulding machine are homogenized and shaped
to form ^{platelets} ~~biscuits~~ [sic]. The inscription with a Nd:YAG
a laser shows a high-contrast black marking with a smooth
surface over a wide range of settings.

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Example 3

- 99 parts of polyamide 6 (Ultramid B3K from BASF)
 1 part of polyimidosulfone milled to a particle size
30 < 15 μm

 The components are mixed and by means of an
injection moulding machine are homogenized and shaped
to form platelets. The inscription with a Nd:YAG laser
shows a high-contrast deep-black marking with a smooth
35 surface over a wide range of settings.

Example 4

- 99.6 parts of polyamide 6 (Ultramid B3K)

0.4 part of polyphenylene sulfide milled to a particle size $< 10 \mu\text{m}$

The components are mixed and by means of an injection moulding machine are homogenized and shaped to form platelets. The inscription with a Nd:YAG laser shows a high-contrast black marking with a smooth surface over a wide range of settings.

Example 5

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99 parts of polyoxymethylene (Delrin from Du Pont)
1 part of polyphenylene sulfide milled to a particle size $< 5 \mu\text{m}$

The components are mixed and by means of an injection moulding machine are homogenized and shaped to form ^{Platelets} biscuits [sic]. The inscription with a Nd:YAG laser shows a high-contrast black marking with a smooth surface over a wide range of settings.

20 Example 6

99 parts of unsaturated polyester resin (Palatal from BASF)

1 part of polyphenylene sulfide milled to a particle size $< 10 \mu\text{m}$

The polyphenylene sulfide is incorporated homogeneously into the liquid polyester casting resin by stirring. Following the addition of accelerator (Co octoate) and hardener (cyclohexanone peroxide), the mixture is poured into a mould. After curing has taken place, a moulding is obtained which can be given a high-contrast black marking by means of Nd:YAG lasers.

Example 7

35 99 parts of polysulfone (Ultrason from BASF) are compounded on an extruder together with 1 part of mica. The compound is micromilled to a particle size of $< 10 \mu\text{m}$. 0.5% of the powder thus obtained are added to a PMMA. This mixture is processed on an extruder to

give sheets which can be given a black and high-contrast marking with a Nd:YAG laser at a wavelength of 532 and 1,064 nm.

5 Example 8

96 parts of polyphenylene sulfide are compounded by the method of Example 7 with 4 parts of basic copper phosphate. An addition of just 0.4% of the micromilled powder of this mixture to commonly non-
10 laser-markable plastics, such as.

- (a) polyethylene (PE)
- (b) polypropylene (PP)
- (c) polyamide (PA)
- 15 (d) ^{polymethyl} ~~methacrylate~~ (PMMA)
- (e) polyurethane (PU)
- (f) polyoxymethylene (POM)

gives deep-black, high-contrast markings with crisp
20 contours using a Nd:YAG laser.